

## DRY CATALYTIC LIQUEFACTION OF A SUBBITUMINOUS COAL: STRUCTURAL INFERENCES

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The catalytic liquefaction of a subbituminous coal has been studied in the absence of solvent using an impregnated sulfided Mo catalyst. Reactions were conducted for various times at temperatures from 300-400°C. The yield and composition of gaseous products, chloroform-soluble liquids and insoluble residue were followed as a function of the reaction conditions, using a number of techniques.

The liquefaction process was divided into two distinct regimes typified by low and high liquid yields (< ca. 10% and > ca. 20%, respectively). Compared to the parent coal, at low yields (realized at 300°C), there was little production of C<sub>1</sub>-C<sub>4</sub> hydrocarbons, a sharp increase in the aliphatic hydrogen content of the liquids and little change in the oxygen functionality of the liquids and residue.

At high yields, C<sub>1</sub>-C<sub>4</sub> production increased and the aliphatic hydrogen content of the liquids was reduced concomitant with an increase in asphaltene content. The oxygen functionality of the liquids and residue also decreased.

Associated changes in the structure and composition of the chloroform-insoluble residue have been further investigated by petrographic analysis and by measurements of swelling in pyridine. The implications are that a large proportion of the coal network structure involves hydrogen-bonded cross linkages.

### INTRODUCTION

In earlier publications, results were presented to describe the application of low-severity catalytic hydrogenation in the absence of added vehicle for providing information on coal structure and liquefaction mechanisms (1-3). In all of these studies the coals were impregnated with a molybdenum disulphide catalyst at a loading of 1% wt Mo (dmmf coal) and reacted at temperatures of 400°C and less, where cracking and condensation reactions will be minimized.

Although the exclusion of solvent undoubtedly creates some disadvantages (e.g. in facilitating catalyst dispersion and eliminating a source of donatable hydrogen) and does not directly relate to liquefaction processing, the past research has shown that this technique offers certain benefits. The derivation of fundamental information is simplified in the absence of solvent and changes in the physical properties of the modified coals and insoluble residues can be measured directly.

The research discussed in this paper describes the results of a study of the low-severity catalytic hydrogenation of a single subbituminous coal at temperatures from 300-400°C. The yield and composition of gaseous, liquid and solid products were followed as a function of reaction time at different temperatures, using several analytical and other techniques. The principal objectives were to provide insight into the two-component coal structural model and the compositional changes associated with liquefaction.

## EXPERIMENTAL

### Coal preparation

The subbituminous coal was obtained from the Penn State Coal Sample Bank. Properties of the coal are shown in Table 1.

The coal samples were crushed to -60 mesh (250 microns) in a glove box in flowing nitrogen and without drying, and were subsequently stored under nitrogen in sealed vials.

The coal was impregnated with molybdenum to a loading of 1% wt Mo (dmmf) using an aqueous solution of a water-soluble molybdenum salt. In order to introduce the catalyst in its most active form ( $\text{MoS}_2$ ) (4,5), an aqueous solution of ammonium heptamolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  was used to produce the thiosalt,  $(\text{NH}_4)_2\text{MoS}_4$ , by reaction with  $\text{H}_2\text{S}$ . The thiosalt decomposes to form  $\text{MoS}_2$  upon mild heating. The procedure has been previously described in detail (1).

### Hydrogenation reaction

Hydrogenation reactions were performed in batch tubing bomb reactors (6). Experiments were conducted at temperatures between 300°C and 400°C for residence times between 5 and 180 min. The bombs were loaded with approximately 3.5-4.5 g of impregnated coal and 0.02 cm<sup>3</sup> of  $\text{CS}_2$  to ensure that the molybdenum was maintained in the fully sulphided form. After flushing, the reactors were pressurized to 7MPa of hydrogen (cold). The reactors were heated by immersion in a preheated fluidized sandbath heater which rapidly raised the reactor contents to the desired temperature. Agitation was provided by vertical oscillation of the reactor through a displacement of 2.5 cm at a frequency of 200 min<sup>-1</sup>. At the end of the reaction period, the reactor was removed from the sandbath and quenched in water.

The gaseous products were collected by venting at room temperature into an evacuated expansion bulb of known volume. Gas samples were analyzed by gas chromatography to determine the yields of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{C}_1$ - $\text{C}_4$  hydrocarbons.

The reaction products remaining in the bomb were rinsed into a pre-dried ceramic thimble with chloroform and extracted overnight in a Soxhlet apparatus. The extract was filtered and the recovered solids were added to those in the Soxhlet thimble. The solvent was removed from the filtrate and the total residue by evaporation under reduced pressure. The extract was dried for 3 h at 100°C in vacuum and the residue for 12 h under the same conditions. The experimental reproducibility for conversion to gases and soluble extract was found to be  $\pm 3\%$ .

The chloroform-solubles were further separated into hexane-solubles (oils) and hexane-insolubles (asphaltenes).

### Product analyses

The liquid products were analyzed for elemental composition, by <sup>1</sup>H NMR spectroscopy (deuterated chloroform solvent; trimethylsilane internal reference), and by Fourier transform infrared spectroscopy (FTIR).

The chloroform-insoluble residues were first derivatized by reaction with acetic anhydride prior to FTIR analysis in order to follow the changes in concentration of -OH groups (7).

The swelling of the residues in pyridine was examined using the procedure described by Liotta et al. (8).

### Optical microscopy

The techniques of microscopic examination and petrographic point-count analysis have been used to follow the processes involved in the hydroliquefaction of various ranks of coal, including subbituminous (9,10). In particular, the efficiency of reaction has been monitored by such features as the proportions of undissolved macerals and the production of insoluble intermediates. In this study, the liquefaction residues (both unextracted and chloroform-insoluble) were embedded in an epoxy resin and polished. Examination was undertaken with a polarizing reflected-light microscope under oil immersion at a magnification of 400. Point-count analyses were performed only on the chloroform-insoluble residues at a magnification of 625; 500 points were counted for each analysis.

Mean reflectance determinations were performed on huminite (vitrinite) and high-reflecting vitroplast.

## RESULTS AND DISCUSSION

### Product yield

The effects of reaction temperature and residence time on the yield of chloroform-solubles produced by dry catalytic hydrogenation is shown in Figure 1.

The extract yields increased with increasing residence time and reaction temperature. At 300°C, the production of chloroform-solubles was low, and even after extended reaction the yield was not much higher than that obtained by Soxhlet extraction of the parent coal (4.4% dmmf). At this temperature, a comparison of catalytic and noncatalytic reactions showed that the presence of the catalyst did not significantly affect the liquid yield.

Higher yields of extract production were measured at 350 and 400°C. After 180 min at 400°C the extract yield was about 65%. Taken together with the gas yield this means that almost 80% of the coal was converted to gaseous and soluble liquid products under these mild reaction conditions. There was little production of light hydrocarbons at low extract yields (< 10%), indicating that there was relatively little cracking at 300°C. The yields of these gases increased at higher conversions.

### Composition of liquids

At low liquid yields (< 10%), there was a sharp increase in the hydrogen content and the H/C atomic ratio of the chloroform-solubles compared to that of the parent coal extract, Figure 2. It was also found that there were corresponding changes in the oil to asphaltene ratio. The ratio increased from a value of 0.8 in the parent coal extract to 8.0 at a yield of about 10% before falling to ca. 1.0 at yields above 20%.

Analyses of the liquids by  $^1\text{H}$  NMR showed that the initial rise in hydrogen content was due to the presence of polymethylene chains. The liberation of long chain alkanes on liquefaction and pyrolysis has been observed by other workers (11-13).

At conversions greater than 20% (liquid yield) the aliphatic hydrogen content was reduced from about 10.5% to 6.5%.

Evidently there is a sharp demarcation between the events which take place at low and at high conversions. In the context of the mobile phase/network concept of coal structure, it can be argued that, for the coal studied here, the observed

boundary represents the limit of the mobile phase, beyond which the additional products derive from the substantial breakdown of the network.

#### Composition and swelling behavior of residues

Analyses of the acetylated residues by FTIR showed that, at low conversions (< 10%), there was little change in the absorption bands attributed to the derivatized -OH groups. Above, about 20% liquid yield, there was a rapid disappearance of -OH groups with increasing conversion.

The change in the swelling ratio of the residues with conversion to chloroform-soluble liquids is shown in Fig. 3. In parallel with the changes in extract composition in going from low to high conversion (as seen by the results of elemental analysis,  $^1\text{H}$  NMR and oil/asphaltene ratio) the swelling ratio increased sharply at low conversion, passed through a maximum and fell to much lower values at conversions greater than 20%. Duplicate experiments confirmed that these data were reproducible.

At low conversions, the FTIR analyses showed that there did not appear to be an appreciable change in the OH content compared to that of the parent coal. The substantial removal of functional groups would be expected to reduce the extent of hydrogen bonding and lower the swelling ratio.

At higher conversions, two factors probably contribute to the reduced swelling, the removal of polar groups and the progressive reduction in the concentration of vitrinite in the residue.

#### Petrographic analysis of residues

The products from the hydrogenation experiments contained the following organic petrographic entities: unreacted huminite (vitrinite) macerals, unreacted liptinite macerals, unreacted inertinite macerals, low-reflecting vitroplast, and high-reflecting vitroplast. Vitroplast is a pitch-like isotropic material which is derived either directly from the melting of vitrinite and other macerals, mainly from coals of bituminous rank, or from the liquid products of dissolution. Low-reflecting vitroplast was observed to have been formed within disintegrating huminite after hydrogenation for 5 min at 400°C. Such material was observed only in the unextracted whole products and is believed to be part of the extractable liquid products; it was no longer present in the residues of chloroform extraction prepared for petrographic point-count analysis. However, certain of these latter residues did contain high-reflecting vitroplast; this material is thought to have been rendered less soluble as a result of thermal treatment.

Table 2 gives the results of the point-count analyses on the chloroform-insoluble residues. It shows that with increasing severity of reaction conditions, liptinite disappears, huminite decreases substantially, inertinite shows an overall increase, and the high-reflecting vitroplast, which appears when the reaction temperature reaches 400°C, also increases. These results suggest a partial explanation for the change in swelling characteristics of the residues illustrated in Fig. 3. The dotted line in this figure represents the swelling which would be shown by the huminite and huminite-derived fraction; it assumes that the inertinite is non-swelling and that the huminite structure is unaltered. This theoretical curve indicates that for the milder conditions (up to 400°C; 5 min), the swelling of the huminitic materials remains high. Only where this material becomes more highly reflecting (Table 2) does the swelling show a substantial decrease (continuous line, Fig. 3). Such residue components together with the inertinite are thought to be depleted in polar side groups and it is this paucity of crosslinks which results in a lowering of the swelling properties. Further, the unreacted huminites in the residues from the more severe treatment conditions have been progressively altered, as shown by their reflectances (Fig. 4). Consequently, oxygen-containing functional

groups would have been gradually eliminated from the huminite structure as a result of the reaction, as supported by the FTIR spectra of the residues.

#### SUMMARY

The results of this research have shown that two regimes of liquefaction can be distinguished.

At low conversion (about 10%) liquids and gases are apparently liberated either through the release of physically trapped materials or through the rupture of weak linkages. Only small quantities of  $C_1$ - $C_4$  hydrocarbons are produced and the extractable liquids are highly paraffinic. There was no significant change in the concentration of functional groups in the chloroform-insoluble products.

At higher conversions (> 20%), there were several notable changes in the composition and properties of the chloroform-soluble liquids and the insoluble residues and an increase in the production of higher hydrocarbon gases. It is considered that the liquids produced at high conversions were substantially derived from the coal network and that the abrupt change in properties between low and high yields is representative of a boundary, based upon behavioral characteristics, between the mobile and network phases.

The results of the swelling experiments suggest that a large proportion of the intra-network cross-linking in this coal involves hydrogen bonding.

Petrographic examination and point-count analysis of the residues shows that huminite (vitrinite) and liptinite are progressively lost as reaction conditions become more severe. This trend is accompanied by increases in the proportions of inertinite and high-reflecting vitroplast, an isotopic pitch-like material generated as a part of the product of dissolution. Although an increase in these latter components would contribute to the decrease in swelling behavior of the residues, it appears that a loss of hydroxyl groups from the huminite is a major factor in this change.

#### ACKNOWLEDGEMENTS

The authors would like to acknowledge the support provided by U.S. Department of Energy under Grant No. DE-FG22-83PC60811 and the Cooperative Program in Coal Research at The Pennsylvania State University.

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TABLE 1  
Coal Properties

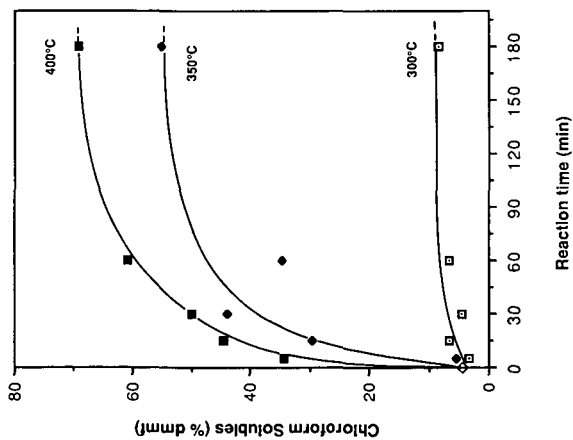
Penn State Sample Bank No.	
Seam	- Anderson
County	- Campbell Co.
State	- Wyoming
Province	- Northern Great Plains
ASTM rank class - sub B.	
Moisture content, % wt (a.r.) - 23.3	
Mineral Matter, % wt dry coal - 11.9*	
<u>Elemental Composition</u> % dmmf	
C	73.0
H	4.5
O**	20.4
N	1.2
S	0.9
<u>Maceral Analysis</u> % vol	
Vitrinite	87
Exinite	2
Inertinite	11
<u>Sulfur Forms</u> (% dry coal)	
Organic	1.2
Pyritic	0.3
Sulfate	0.05
Total	1.55

\*Reported as ASTM "Ash"

\*\*By Difference

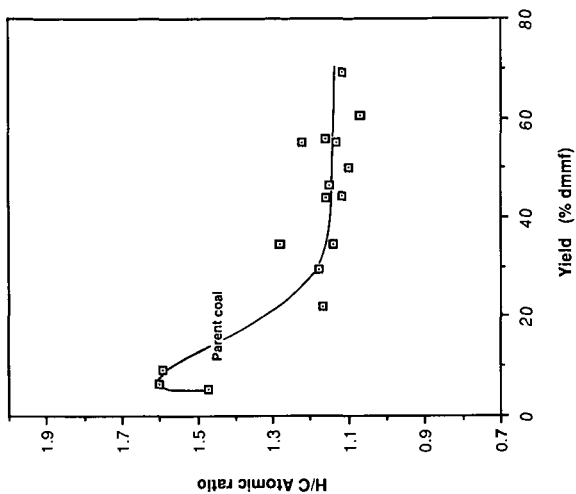
TABLE 2  
Petrographic Analyses of Chloroform-insoluble Residues

Temperature °C	Time min.	Yield	Unreacted Huminite, %	Unreacted Liptinite, %	Unreacted Inertinite, %	High-Reflecting Vitroplast, %
300	5	3.37	87	8	5	0
300	60	6.46	86	7	7	0
350	60	34.69	85	6	9	0
400	15	44.47	63	0	10	27
400	30	50.09	55	0	12	33
400	60	60.65	41	0	8	51



CHLOROFORM-SOLUBLES YIELD AS A FUNCTION OF TEMPERATURE AND REACTION TIME  
(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPA  $H_2$ , COLD; 1% WT MO)

FIGURE 1



VARIATION OF THE H/C ATOMIC RATIO AS A FUNCTION OF CONVERSION YIELDS  
(SUBBITUMINOUS COAL (PSOC-1403P); 7 MPA  $H_2$ , COLD; 1% WT MO)

FIGURE 2



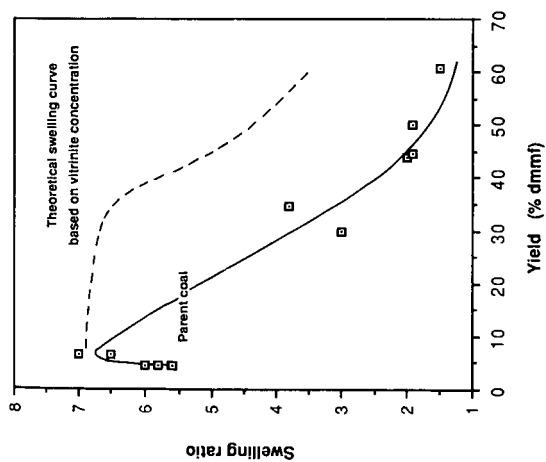


FIGURE 3  
VARIATION OF THE SWELLING RATIO OF  
CHLOROFORM-EXTRACTED RESIDUES WITH  
CHLOROFORM-SOLUBLES YIELD  
(SUBBITUMINOUS COAL (PSOC-1430P); 7 MPa H<sub>2</sub>,  
COLD; 1% wt Mo)

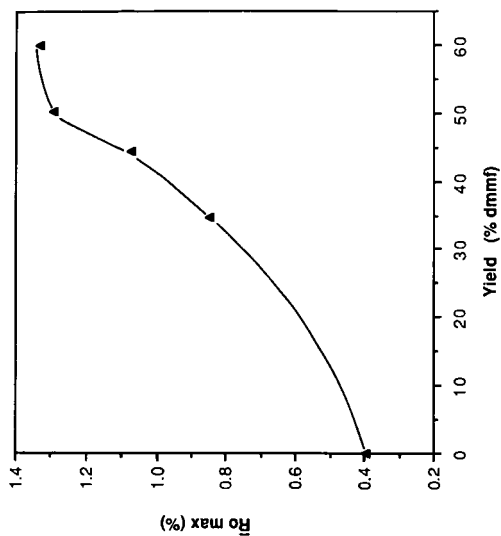


FIGURE 4  
VARIATION IN MEAN MAXIMUM REFLECTANCE OF  
HUMINITE (VITRINITE) AND VITROPLAST RESIDUE  
COMPONENTS WITH CHLOROFORM-SOLUBLES YIELD